



Short communication

Sulfur/three-dimensional graphene composite for high performance lithium–sulfur batteries



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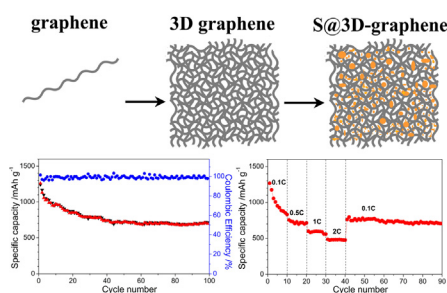
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HIGHLIGHTS

- Three-dimensional graphene is assembled by a simple hydrothermal reduction.
- The 3D graphene shows a hierarchical porous morphology and robust structure.
- Sulfur content up to 73% is loaded in 3D graphene.
- The composite shows high specific capacity and stable capacity retention.
- The unique 3D structure enables high-rate capability.

GRAPHICAL ABSTRACT



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ABSTRACT

A sulfur/graphene composite is prepared by loading elemental sulfur into three-dimensional graphene (3D graphene), which is assembled using a metal ions assisted hydrothermal method. When used as cathode materials for lithium–sulfur (Li–S) batteries, the sulfur/graphene composite (S@3D-graphene) with 73 wt % sulfur shows a significantly enhanced cycling performance ($>700 \text{ mAh g}^{-1}$ after 100 cycles at 0.1C rate with a Coulombic efficiency $> 96\%$) as well as high rate capability with a capacity up to 500 mAh g^{-1} at 2C rate (3.35 A g^{-1}). The superior electrochemical performance could be attributed to the highly porous structure of three-dimensional graphene that not only enables stable and continue pathway for rapid electron and ion transportation, but also restrain soluble polysulfides and suppress the “shuttle effect”. Moreover, the robust structure of 3D graphene can keep cathode integrity and accommodate the volume change during high-rate charge/discharge processes, making it a promising candidate as cathode for high performance Li–S batteries.

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1. Introduction

Elemental sulfur delivers a high theoretical specific capacity of 1675 mAh g^{-1} versus lithium, which is seven times higher than that of the intercalation cathode materials used in lithium-ion batteries, making lithium–sulfur (Li–S) battery the promising candidate for electric vehicles and energy storage systems for renewable energy

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[1,2]. Sulfur is also environmentally friendly, economical and abundant. However, in spite of its attracting properties, Li–S battery suffers severe capacity decay because of the poor conductivity of sulfur, the dissolution of intermediate lithium polysulfide products Li_2S_n ($2 < n \leq 8$) along with “shuttle effect”, the precipitation of insoluble and insulating $\text{Li}_2\text{S}_2/\text{Li}_2\text{S}$ on the electrodes and volumetric expansion [3,4]. Considering these drawbacks, the most attractive strategy is to create nanocomposites containing sulfur, among which conductive materials have been a popular choice. Many pioneering work have been made to combine sulfur with conductive materials such as carbon nanotube [5–7], porous carbon [8–10], conducting polymers [11–15], graphene and graphene oxide [3,16,17].

As one of the most promising conductive additives, graphene has significant advantages of high specific surface area, superior electron mobility and good chemical stability [18]. It has been demonstrated that graphene is an outstanding cathode support for Li–S batteries to improve the electronic conductivity and the utilization of sulfur [16,17,19–21]. However, graphene fails to trap the polysulfides due to its open structure, resulting in low Coulombic efficiency and limited cyclic stability. Therefore, it is urgent to construct a three-dimensional structure of graphene that provides highly conducting network for charge transfer, flexible space accommodating the volumetric expansion during cycling as well as porous morphology to immobilize the polysulfide species [3]. Though 3D graphene has been used in lithium ion batteries, to the best of our knowledge, there are few reports focusing on the application of 3D graphene in Li–S batteries [22,23].

Herein, we report a simple method to prepare three-dimensional graphene supported sulfur composite (S@3D-graphene) as cathode material for Li–S battery. Due to its robust and highly porous 3D-connected structure, the composite showed superior electrochemical performance.

2. Experimental

Graphene oxide (GO) was prepared by a modified Hummer's method [24]. 3D graphene is assembled by Co^{2+} assisted-hydrothermal reduction [25]. Briefly, 100 ml 1 g L^{-1} GO solution was mixed with 2.2 mg CoCl_2 and then transferred into a Teflon-lined stainless steel autoclave and heated at 120°C for 10 h. After that, cylindrical precipitate was collected and washed 3 times by deionized water followed by vacuum freeze drying. The obtained cylindrical 3D graphene was cut to small pieces, ground with sulfur powder and heated for 12 h at 155°C to form a homogeneously mixed S@3D-graphene composite.

Powder X-ray diffraction (XRD, $\text{Cu K}\alpha$ radiation, Philips PW3040/60) was used to verify the structure of the composite.

Sulfur content in the S@3D-graphene was determined by thermogravimetric/differential thermal analysis (TG/DTA) (Netzsch STA 449C thermal analyzer). The morphologies were examined by scanning electron microscopy (SEM, Hitachi S-4800), and transmission electron microscopy (TEM, JEOL 2100F).

The electrodes were prepared by dispersing the S@3D-graphene composite (75 wt %), acetylene carbon black (15 wt %) and polyvinylidene fluoride binder (10 wt %) in N-methyl-2-pyrrolidone solvent to form a slurry. The slurry was pasted onto aluminum foils and dried at 60°C for 12 h in a vacuum oven. Two-electrode CR2032-type coin cells with a lithium foil as the counter electrode and Celgard 2400 as the separator were assembled in an argon-filled glove box. The electrolyte solution was 1 M lithium bis(trifluoromethane sulfonimide) (LiTFSI), 0.1 M LiNO_3 in a solvent of 1,3-dioxolane (DOL): 1,2-dimethoxyethane (DME) with a volume ratio of 1: 1. Cyclic voltammetry (CV) was carried out on a CHI 604D electrochemistry workstation (Shanghai Chenhua Instruments Co. Ltd.) from 1.5 to 3.0 V at a scan rate of 0.1 mV s^{-1} . The galvanostatic charge and discharge measurements were performed on a battery test system (Shenzhen Neware Tech. Ltd.) at different current densities in the voltage range from 1.5 to 3.0 V.

3. Result and discussion

Fig. 1a shows the thermogravimetric (TG) curves of the elemental sulfur and S@3D-graphene composite. It is found that sulfur starts to evaporate at about 220°C and losses the weight completely above 350°C . The gradual weight loss above 400°C for the S@3D-graphene composite is attributed to the decomposition of oxygen-containing functional groups on the surface of graphene. As determined by TG method, the content of sulfur in the composite is calculated to be 73%. This loading mass is quite satisfied, since it is well-accepted that the content of sulfur should exceed 50% for practical use [26]. Fig. 1b shows the XRD patterns of the elemental sulfur, the 3D graphene, and the as-produced S@3D-graphene composite. Comparing with the elemental sulfur, the characteristic peaks of orthorhombic sulfur (JCPDS No. 77-0145) in the S@3D-graphene composite become weak, indicating poor crystallinity of sulfur which is infiltrated in the graphene networks. Besides, the broadened characteristic peak of graphene at 24.3° is also observed.

The morphology of the S@3D-graphene composite is observed by SEM and TEM (Fig. 2). SEM image (Fig. 2a) of the S@3D-graphene composite shows that the 3D graphene with a highly porous hierarchical structure is composed of wrinkled and three-dimensionally connected graphene nanosheets. It is worthy to mention that the as-prepared cylinder-shaped 3D graphene exhibits good flexibility and strength, suggesting a robust structure

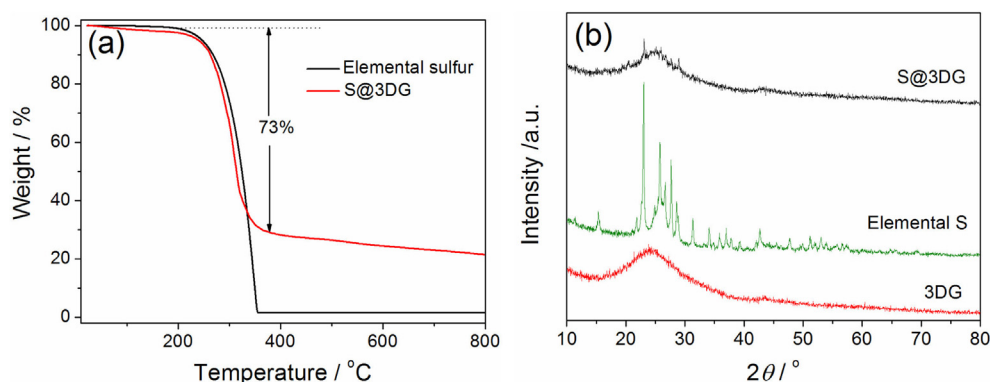


Fig. 1. (a) Thermogravimetric curves of the S@3D-graphene composite and elemental sulfur; (b) XRD patterns of 3D graphene, elemental sulfur and the S@3D-graphene composite.

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